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PRIORITY DATE CLAIMED

TITLE OF INVENTION

HERBICIDALLY ACTIVE PYRIDINE SULFONYL UREA DERIVATIVES

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Applicant herewith submits to the United States Designated/Elected Office (DO/EO/US) the following items and other information:

1. ☒ This is a **FIRST** submission of items concerning a filing under 35 U.S.C. 371.
2. ☐ This is a **SECOND** or **SUBSEQUENT** submission of items concerning a filing under 35 U.S.C. 371.
3. ☒ This is an express request to begin national examination procedures (35 U.S.C. 371(f)). The submission must include items (5), (6), (9) and (24) indicated below.
4. ☐ The US has been elected by the expiration of 19 months from the priority date (Article 31).
5. ☒ A copy of the International Application as filed (35 U.S.C. 371 (c) (2)) **PCT/KR00/01138**
 - a. ☐ is attached hereto (required only if not communicated by the International Bureau).
 - b. ☒ has been communicated by the International Bureau.
 - c. ☐ is not required, as the application was filed in the United States Receiving Office (RO/US).
6. ☒ An English language translation of the International Application as filed (35 U.S.C. 371(c)(2)).
 - a. ☒ is attached hereto.
 - b. ☐ has been previously submitted under 35 U.S.C. 154(d)(4).
7. ☒ Amendments to the claims of the International Application under PCT Article 19 (35 U.S.C. 371 (c)(3))
 - a. ☐ are attached hereto (required only if not communicated by the International Bureau).
 - b. ☐ have been communicated by the International Bureau.
 - c. ☐ have not been made; however, the time limit for making such amendments has NOT expired.
 - d. ☒ have not been made and will not be made.
8. ☐ An English language translation of the amendments to the claims under PCT Article 19 (35 U.S.C. 371(c)(3)).
9. ☒ An oath or declaration of the inventor(s) (35 U.S.C. 371 (c)(4)).
10. ☐ An English language translation of the annexes to the International Preliminary Examination Report under PCT Article 36 (35 U.S.C. 371 (c)(5)).
11. ☐ A copy of the International Preliminary Examination Report (PCT/IPEA/409).
12. ☒ A copy of the International Search Report (PCT/ISA/210).

Items 13 to 20 below concern document(s) or information included:

13. ☐ An Information Disclosure Statement under 37 CFR 1.97 and 1.98.
14. ☒ An assignment document for recording. A separate cover sheet in compliance with 37 CFR 3.28 and 3.31 is included.
15. ☐ A **FIRST** preliminary amendment.
16. ☐ A **SECOND** or **SUBSEQUENT** preliminary amendment.
17. ☐ A substitute specification.
18. ☐ A change of power of attorney and/or address letter.
19. ☐ A computer-readable form of the sequence listing in accordance with PCT Rule 13ter.2 and 35 U.S.C. 1.821 - 1.825.
20. ☐ A second copy of the published international application under 35 U.S.C. 154(d)(4).
21. ☐ A second copy of the English language translation of the international application under 35 U.S.C. 154(d)(4).
22. ☒ Certificate of Mailing by Express Mail **Label No. : EL932682353US**
23. ☒ Other items or information:

Copy of Applicants' letter dated Aug. 20, 2001 to the IB

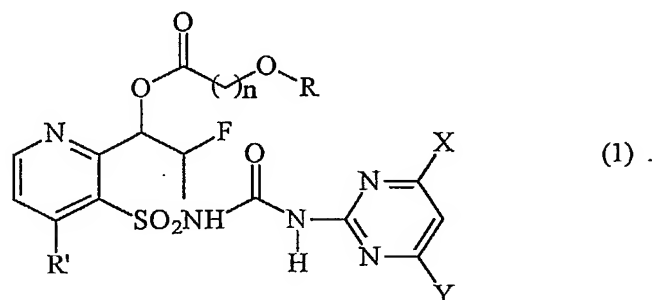
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HERBICIDALLY ACTIVE
PYRIDINE SULFONYL UREA DERIVATIVES

TECHNICAL FIELD

The present invention relates to pyridine sulfonyl urea derivatives represented by the following formula (1):



in which

n denotes an integer of from 1 to 3,

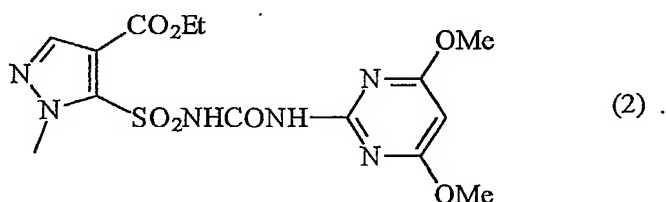
R represents H or C₁-C₄-alkyl,

R' represents H, C₁-C₄-alkyl, C₁-C₃-haloalkyl, halogen, or C₁-C₂-alkoxy, and

X and Y independently of one another represent C₁-C₂-alkyl, C₁-C₂-alkoxy, C₁-C₂-haloalkoxy, or halogen, salts or stereochemical isomers thereof showing an effective herbicidal activity in pre- and/or post-emergence treatment in rice farming, or to a method to use thereof, a method for the preparation thereof, an intermediate used for the preparation thereof, and a herbicidal composition comprising same.

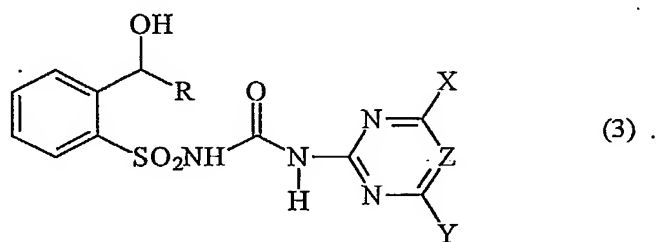
BACKGROUND ART

Hitherto, there have been reported a lot of sulfonyl urea derivatives having a
 5 herbicidal activity in rice farming. For example, JP 61/191602 discloses a compound
 represented by the following formula (2):



, which has been commercialized as a herbicide for rice farming in the name of
 10 Pyrazosulfuron-ethyl.

Korean Patent No. 70675 discloses a compound represented by the following
 formula (3):



15 in which

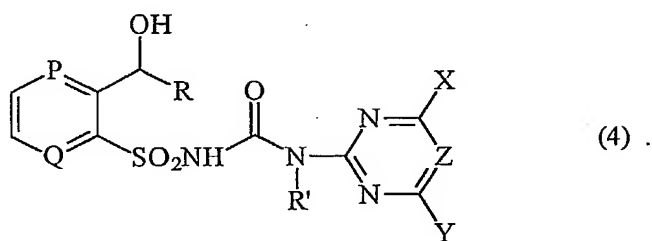
R represents haloalkyl,

X and Y independently of one another represent CH₃, OCH₃, Cl, etc., and

Z represents CH or N.

20 Korean Patent Application No. 91-3014 discloses a herbicidally active sulfonyl

urea derivative represented by the following formula (4):



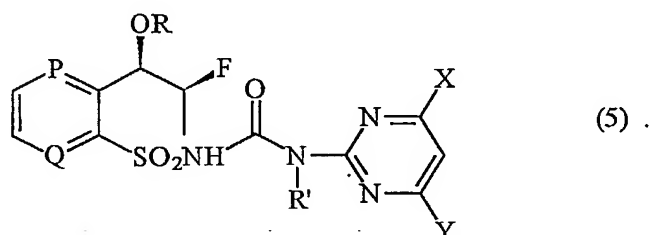
in which

5 R, X, Y and Z are defined as the above formula (3),

R' represents H or CH₃, and

P and Q independently of one another represent CH or N, but where the aromatic ring including P and Q is benzene or pyridine.

10 Korean Patent Application No. 93-6915 discloses a herbicidally active pyridine sulfonyl urea derivative represented by the following formula (5):



in which

P, Q, R', X and Y are defined as in the above formula (4),

15 R represents H, R^a-(C=O)- or R^a-X^a-(C=O)-, wherein R^a represents C₁~C₄-alkyl, C₁~C₃-haloalkyl, C₂~C₄-alkenyl or C₂~C₄-alkynyl, and X^a represents O, S, NH or NR^a.

The existing sulfonyl urea-based herbicidal compounds as explained above show an excellent herbicidal activity against annual and perennial weeds in rice, but have weak

activity to barnyardgrass which is the most problematic weed in rice, or cause some phytotoxicity to rice plant. The present inventors claim new pyridine sulfonyl urea derivatives having improved rice safety and superior herbicidal activity against barnyardgrass to the earlier herbicidal compounds, and find great advantages of these new compounds when used as a rice herbicide.

Therefore, one object of the present invention is to provide the pyridine sulfonyl urea derivatives of the above formula (1), salts or stereochemical isomers thereof.

It is another object of the present invention to provide a process for the preparation of the compound of formula (1).

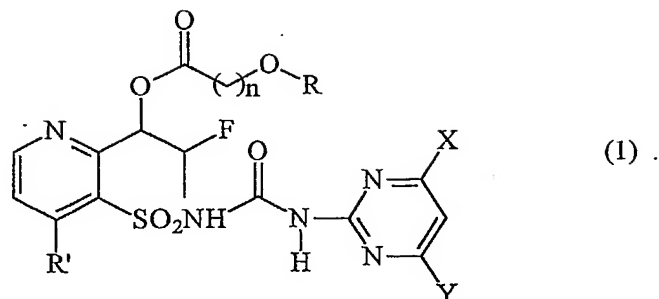
It is further object of the present invention to provide a novel intermediate which is used for the preparation of the compound of formula (1).

It is further object of the present invention to provide a method to use the compound of formula (1) as a herbicide for paddy rice, and a herbicidal composition comprising same.

The present invention will be explained in more detail hereinafter.

DISCLOSURE OF INVENTION

The present invention relates to a compound of the following formula (1):



in which

n denotes an integer of from 1 to 3,

R represents H or C₁-C₄-alkyl,

5 R' represents H, C₁-C₄-alkyl, C₁-C₃-haloalkyl, halogen, or C₁-C₂-alkoxy, and

X and Y independently of one another represent C₁-C₂-alkyl, C₁-C₂-alkoxy, C₁-C₂-haloalkoxy, or halogen.

Among the compound of formula (1) which shows an excellent selectivity to rice
 10 plant and herbicidal activity to barnyardgrass and thus, can be advantageously used as a
 herbicide for rice farming, the preferred compounds include those wherein n denotes an
 integer of 1 or 2, R represents H or methyl, R' represents H, halogen or methyl, and X and
 Y each represents methoxy.

15 Particularly preferred compounds include those wherein n denotes an integer of 1
 or 2, R represents methyl, R' represents H, Cl, Br or methyl, and X and Y each represents
 methoxy.

Typical examples of the compound of formula (1) according to the present
 20 invention are exemplified as follows:

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-methoxy acetoxyn-propyl)pyridine-3-sulfonamide.

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy acetoxyn-propyl)pyridine-3-sulfonamide.

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-(3-hydroxy propion)oxy-n-propyl)pyridine-3-sulfonamide.

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-(3-methoxypropion)oxy-n-propyl)pyridine-3-sulfonamide.

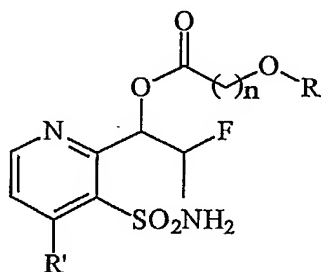
5 N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-4-methyl-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide.

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-4-chloro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide.

10 N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-4-bromo-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide.

Since the compound of formula (1) has two asymmetric carbons therein, they can exist as an erythro or threo isomer, or mixtures thereof. The compound of the present invention shows a stronger activity in the erythro form, but the mixtures thereof in a
15 suitable mixing ratio also exhibit a sufficient activity.

The compound of formula (1) according to the present invention can be prepared by a process characterized in that a compound represented by the following formula (6):

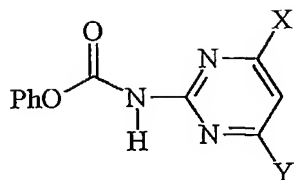


(6)

20 in which

n, R and R' are defined as in the above formula (1), is reacted in a solvent optionally in the presence of a base with a compound represented by the following formula (7):

7



(7)

in which

X and Y are defined as in the above formula (1). Therefore, it is another object of the present invention to provide such a preparation process.

5

The compound of formula (6) used as a starting material in the process according to the present invention can exist as an erythro isomer, threo isomer, or mixtures thereof. The stereo-chemical configuration of the desired compound of formula (1) may be determined in line with the configuration of compound (6).

10

Any solvent which does not adversely affect the reaction can be used in the above process, but preferably tetrahydrofuran, acetone, acetonitrile, dioxane, methylene chloride, toluene, butanol, pyridine, dimethylformamide, etc. can be used. The above process is carried out preferably in the presence of a small amount of strong base, such as for example, triethylamine, hexamethylenetetramine, pyridine, DBU or DABCO (wherein DBU means 1,8-diazabicyclo[5,4,0]undec-7-ene and DABCO means 1,4-diazabicyclo[2,2,2]octane, and they have the same meaning throughout the present specification), etc., and the reaction temperature may be preferably maintained in the range of 10~80°C. The specific reaction conditions can be referred to USP 4,443,245 which discusses similar reactions, and after the reaction is completed, the desired compound can be obtained through the acid-treatment procedure as described in EP 044,807. If a highly pure compound is required, it is desirable to use HPLC technique.

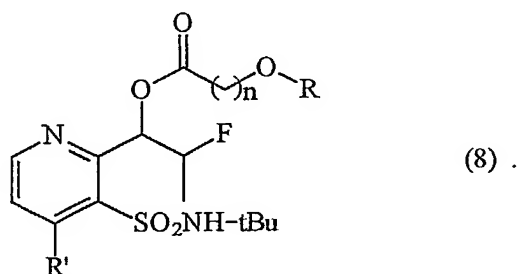
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25

The compound of formula (7) was known and can be easily prepared according to the process described in Korean Patent No. 70,675.

The compound of formula (6) is a novel intermediate which is provided first by the present invention. Therefore, it is another subject matter to be provided by the present invention. The compound of formula (6) can be prepared by treating a compound represented by the following formula (8):

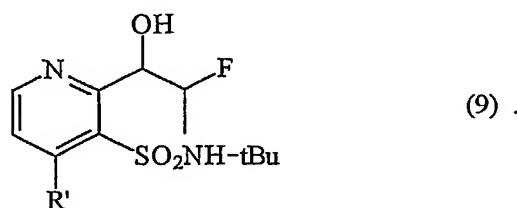


5

in which, n, R and R' are defined as formula (1), with trifluoroacetic acid (TFA) to eliminate the t-butyl group therefrom.

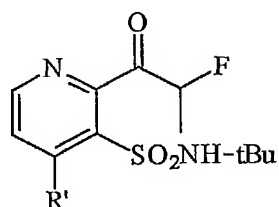
If the compound of formula (8) is stirred in the solvent of trifluoroacetic acid (TFA) at 0~80°C, the t-butyl group is eliminated to give the sulfonamide compound of formula (6). When the compound of formula (6) thus obtained is present in the form of an erythro-threo mixture, it may be resolved by column chromatography, HPLC or preparative-TLC method to give pure erythro or threo compound.

The compound of formula (8) may also be prepared by acylating a compound represented by the following formula (9) according to a conventional manner:



in which R' is defined as in the above formula (1).

The compound of formula (9) may be prepared by selectively reducing a compound represented by the following formula (10):



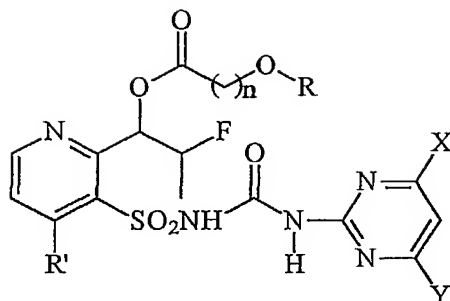
(10) .

5

in which R' is defined as in the above formula (1), using a suitable reducing agent, such as for example, DIBAL-H (Diisobutylaluminum hydride), NaBH_4 , LiAlH_4 , BH_3 .

The compound of formula (1) as can be prepared as explained above is more
10 definitely exemplified individually in the following Table 1.

15



[Table 1]

R'	n	R	X	Y	m.p.(°C)
Cl	1	CH ₂	Ome	OMe	135-140
Br	1	CH ₃	Ome	OMe	87-89
Br	1	H	Ome	OMe	
OCH ₃	1	CH ₃	Ome	OMe	
CH ₃	1	CH ₃	Ome	OMe	156-158
CF ₃	1	CH ₃	Ome	OMe	
H	1	H	Ome	OMe	157-158
CH ₃	2	CH ₃	Ome	OMe	
H	1	CH ₃	Ome	OMe	175-177(erythro)
H	1	CH ₃	Ome	OMe	152-154(threo)
H	1	CH ₃	Ome	Cl	
H	1	CH ₃	Me	Me	
H	2	H	Ome	OMe	147-148
H	2	CH ₃	Ome	OMe	145-146

The compound of formula (1) according to the present invention may exist as a suitable salt and is utilizable as a herbicide in that form. The salt can be prepared by a conventional method known per se, for example, by contacting the compound of formula (1) with a solution containing hydroxide, alkoxide, or carbonate of alkali metal or alkaline earth metal. Otherwise, the salt may be prepared by using an amine compound in the similar manner.

Various salts can also be obtained by exchanging the cation of the salt of compound of formula (1) by another one. Cation exchange is carried out by directly contacting a salt of the compound of formula (1), for example, alkali metal salt or quarternary amine salt in aqueous solution with a solution containing the cation to be

newly combined. This method is the most effective when the resulting salt containing the newly combined cation is insoluble in water. Ion exchange can also be carried out by subjecting a salt of the compound of formula (1), for example, alkali metal salt or quarternary amine salt in aqueous solution to a column filled with cation exchange resin
5 containing the cation to be newly combined. In this case, the cation in the resin is exchanged with the cation of the original salt and the desired salt newly formed is eluted from the column. This method is particularly effective when the resulting salt is water-soluble, that is, sodium, potassium or calcium salt.

10 Further, the compound of formula (1) is conveniently used as a herbicidal agent when it is present in the form of mixtures or complexes with urea or amide compound. Those mixtures or complexes may be prepared according to the typical methods.

The preparation or conversion process as briefly summarized above may be easily
15 carried out by a person skilled in the area of organic synthesis or synthesis of sulfonyl urea derivatives. All the processes designed from the present description by conventional modifications fall within the scope of the present invention.

As stated already, the pyridine sulfonyl urea derivative of formula (1) according to
20 the present invention can be used as a herbicidal agent. Therefore, the utilities and formulations are explained below.

[Utility]

25 Since the compound of formula (1) has an excellent selectivity for rice plant as well as a potent herbicidal activity, it can be used as a herbicide for paddy rice and can be contained as an active ingredient in herbicidal composition.

Test results indicate that the compound of formula (1) is highly active as a
30 herbicide for pre- or post-emergence treatment in paddy and upland.

The rates of application of the active compound of the invention are determined by a number of factors, including the types of weeds to be controlled, weather, climate, formulations selected, mode of application, size of weeds, etc. In general terms, the subject compounds should be applied at levels of around 1g to 1 kg/ha, the lower rates being suggested for use on soils having a low organic matter content or sandy soil, for young plants, or for situations where only short-term persistence is required. Particularly, the subject compounds may be used effectively in rice to control various weeds including barnyardgrass, annual broadleaf and sedge weeds as well as perennial weeds.

The compounds of the present invention may be used alone or as two-, three-, or four-way combinations together with the existing herbicides.

15 [Formulation]

In the present invention, the compound of formula (1) is used in the form of a conventional composition. If necessary, the compound of formula (1) is applied to plant, soil, or water surface in combination with carriers, surfactants, adjuvants, or other additives which are conveniently used in the technical field of formulation.

Suitable carriers and additives may be a solid or a liquid and include those components effectively used in the field of formulation, such as for example, natural or synthetic inorganic substances, solvents, dispersants, wetting agents, adhesive agents, thickening agents, binding agents, etc.

The composition comprising the compound of formula (1) is preferably applied to soil in the form of a solid, for example, a granule, or liquid (soil treatment). Otherwise, the composition comprising the compound of formula (1) may be applied directly to a plant foliage (foliar treatment). Frequency and rate of application are varied depending

on the biological characteristics of plants, weather, soil types, and other environmental conditions.

The active ingredient-containing combinations in unmodified form can be used
5 together with the known adjuvants conveniently used in the field of formulation. They
are formulated according to the known methods to emulsifiable concentrates, liquid
formulations which can be diluted, liquid hydrates which can be directly applied to water
surface, developing agent for water surface, emulsions, hydrates, powders, dusts, granules
or tablets. Application methods such as spraying, dusting, broadcasting, etc. and
10 characteristics of the composition are selected to be compatible with the purpose of use and
environments. The rate of application of the active ingredient-containing combination
varies generally in the range of from 1g to 1kg a.i./ha, preferably from 10g to 30g a.i./ha.

For example, the active ingredient may be intimately mixed and/or pulverized with
15 extenders[e.g. solvents, solid carriers and if desired, surface-active compounds
(surfactants)] according to the known methods to give the combinations.

Possible solvents include the following: aromatic hydrocarbons such as xylene
mixtures or substituted naphthalenes; alcohols and glycols, and their ethers and esters such
20 as ethanol, ethylene glycol, ethylene glycol monomethyl or monoethyl ether; ketones such
as cyclohexanone; strongly polar solvents such as N-methyl-2-pyrrolidone,
dimethylsulfoxide or dimethylformamide; optionally epoxidised vegetable oils such as
epoxidised coconut oil or soybean oil; and water. These solvents can be used as
emulsifying agents, solvents for liquid formulation or cosolvents for granule formulation.

25

The solid carriers used e.g. for dusts and granules, are normally pulverized natural
mineral fillers such as talc, kaolin, montmorillonite, pyrophyllite, bentonite, calcite, or
adsorptive carriers such as zeolite, or sand. In addition, a great number of prepulverized
materials of inorganic or organic nature can be used.

30

Depending on the nature of the compound of formula (1) to be formulated, suitable surface-active compounds are nonionic, cationic and/or anionic surfactants having good dispersing, wetting and lubricating properties. The term "surfactants" will also be understood as comprising mixtures of surfactants.

The herbicidal compositions, broadly, contain 0.1 to 99% by weight, preferably 0.1 to 95% by weight of the compound of formula (1), 99.9 to 1% by weight, preferably 99.9 to 5% by weight of solid or liquid additives, and 0 to 25% by weight, preferably 0.1 to 25% by weight of surfactant.

These compositions fall within the scope of the present invention.

BEST MODE FOR CARRYING OUT THE INVENTION

The process for the preparation and use of the compound according to the present invention will be more specifically explained in the following Examples. However, it should be understood that these Examples are intended to illustrate the present invention but not in any manner to limit the scope of the present invention. Unless otherwise stated, C18 silica(25-40 μ m, 50ml) column equilibrated with acetonitrile/water=10/90(v/v) was used as the stationary phase of column chromatography in the following Examples.

Example 1: Synthesis of erythro-N-t-butyl-4-methyl-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide

Erythro-N-t-butyl-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide (2.55g) was dissolved in THF(150ml) which had been well purified and then 2.5N n-BuLi(13.4ml) was slowly added thereto under nitrogen gas at -78°C. The reaction temperature was raised to -20°C and cooled down to -78°C again. CuI(2.10g) was introduced into

another flask and the lithium salt prepared above was reversely added to this flask. After 10 minutes, CH_3I (0.83ml) was added, the resulting mixture was stirred for 30 minutes at -78°C , and the reaction was quenched with NH_4Cl solution. Ethyl acetate was added to the reaction solution to separate the organic layer. The aqueous layer was
5 extracted with ethyl acetate, and then the organic layers were combined, dried(MgSO_4), filtered and concentrated to give a crude product. This crude product was subjected to column chromatography (Moving phase: ethyl acetate/n-hexane=1/2, v/v) to give 0.5g of the pure title compound.

10 ^1H NMR(200MHz, CDCl_3) : δ 8.55(d, 1H, $J=5\text{Hz}$), 7.24(d, 1H, $J=5\text{Hz}$), 6.1 (br s, 1H), 4.6~4.9(m, 3H), 2.76(s, 3H), 1.35(dd, 3H, $J_1=25\text{Hz}$, $J_2=6\text{Hz}$), 1.26 (s, 9H)

Example 2: Synthesis of erythro-4-methyl-2-(2-fluoro-1-methoxy- acetoxy-n-propyl)pyridine-3-sulfonamide

15

Erythro-N-t-butyl-4-methyl-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide(0.7g) was dissolved in THF(10ml) and methoxyacetylchloride(0.32g) was added thereto. 60% NaH(0.13g) was added at 0°C and the resulting mixture was stirred for 2 hours at room temperature. The reaction was quenched with saturated aqueous NH_4Cl
20 solution and extracted with ethyl acetate. The organic layer was dried(MgSO_4), filtered and concentrated, and the residue was subjected to column chromatography(Moving phase: ethyl acetate/n-hexane=1/3, v/v) to give erythro-N-t-butyl-4-methyl-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide(0.7g).

25

To the resulting product was added $\text{CF}_3\text{CO}_2\text{H}$ (10ml) and the mixture was stirred for 1 hour at $60\sim 65^\circ\text{C}$. The reaction solution was concentrated under reduced pressure and the residue was dissolved in methylene chloride and washed with aqueous sodium bicarbonate solution. The organic layer was dried(MgSO_4), filtered and concentrated, and the residue was subjected to column chromatography (Moving phase: ethyl
30 acetate/methylene chloride=1/7→ 1/1, v/v) to give 0.37g of the pure title compound.

¹H NMR(200MHz, CDCl₃) : δ 8.57(d, 1H, J=5Hz), 7.24(d, 1H, J=5Hz), 6.85 ~ 6.95(m, 1H), 5.65(br s, 2H), 4.9 ~ 5.3(m, 1H), 4.13(s, 2H), 3.41(s, 2H), 2.72(s, 3H), 1.55(dd, 3H, J₁=25Hz, J₂=6Hz)

5

Example 3: Synthesis of erythro-N-t-butyl-4-chloro-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide

Erythro-N-t-butyl-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide(0.29g)
10 was dissolved in THF(10ml) which had been well purified and then 2.5N n-BuLi(1.52ml) was slowly added thereto under nitrogen gas at -78°C. The reaction temperature was raised to -20°C and cooled down to -78°C again. NCS(N-chlorosuccinimide)(0.2g) dissolved in THF(5ml) was slowly added to the reaction solution. After 30 minutes, the reaction was quenched with saturated aqueous ammonium chloride solution. Ethyl
15 acetate was added to the reaction solution to separate the organic layer. The aqueous layer was extracted once more with ethyl acetate, and then the organic layers were combined, dried (MgSO₄), filtered and concentrated to give a crude product. This crude product was subjected to column chromatography (Moving phase: ethyl acetate/n-hexane=1/2, v/v) to give 0.18g of the pure title compound.

20

¹H NMR(200MHz, CDCl₃) : δ 8.61(d, 1H, J=5Hz), 7.50(d, 1H, J=5Hz), 6.05 ~ 6.15(br s, 1H), 5.2(br s, 1H), 4.6 ~ 4.9(m, 2H), 1.35(dd, 3H, J₁=25Hz, J₂=6Hz), 1.25(s, 9H)

Example 4: Synthesis of erythro-N-t-butyl-4-chloro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide

25

Erythro-N-t-butyl-4-chloro-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide(0.75g) was dissolved in THF(10ml) and methoxyacetylchloride(0.33g) was added thereto. The reaction solution was cooled down to 0°C and 60% NaH (0.13g) was
30 added. The resulting solution was warmed to room temperature and stirred for 2 hours.

The reaction was quenched with aqueous ammonium chloride solution. The reaction solution was extracted with ethyl acetate and the organic layer was dried (MgSO₄), filtered and concentrated. The residue was subjected to column chromatography (Moving phase: ethyl acetate/n-hexane=1/3, v/v) to give 0.7g of the pure title compound.

5

¹H NMR(200MHz, CDCl₃) : δ 8.60(d, 1H, J=5Hz), 7.46(d, 1H, J=5Hz), 7.05 ~ 7.15(m, 1H), 5.45(br s, 1H), 4.9 ~ 5.3(m, 1H), 2.1(s, 3H), 1.44(dd, 3H, J₁=25Hz, J₂=6Hz), 1.31(s, 9H)

10

Example 5: Synthesis of erythro-N-t-butyl-4-bromo-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide

15

Erythro-N-t-butyl-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide(7.0g) was dissolved in THF(200ml) which had been well purified and then 2.5N n-BuLi (13.4ml) was slowly added thereto under nitrogen gas at -78°C. The reaction temperature was raised to -20°C and cooled down to -78°C again. NBS(N-bromosuccinimide)(6.4g) was added to the reaction solution and the resulting mixture was stirred for 30minutes. The reaction was quenched with saturated aqueous ammonium chloride solution. Ethyl acetate was added to the reaction solution to separate the organic layer. The aqueous layer was extracted once more with ethyl acetate, and then the organic layers were combined, dried (MgSO₄), filtered and concentrated to give a crude product. This crude product was subjected to column chromatography (Moving phase: ethyl acetate/n-hexane=1/2, v/v) to give 3.9g of the pure title compound.

25

¹H NMR(200MHz, CDCl₃) : δ 8.48(d, 1H, J=5Hz), 7.74(d, 1H, J=5Hz), 6.5(br s, 1H), 5.39(br s, 1H), 4.6 ~ 4.95(m, 2H), 1.32(dd, 3H, J₁=25Hz, J₂=6Hz), 1.25(s, 9H)

Example 6: Synthesis of erythro-4-bromo-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide

30

Erythro-N-t-butyl-4-bromo-2-(2-fluoro-1-hydroxy-n-propyl)pyridine-3-sulfonamide(0.5g) was dissolved in trifluoroacetic acid(CF₃CO₂H; 10ml) and the resulting solution was stirred for 2 hours at 60~65°C. The reaction solution was concentrated under reduced pressure, and then the filtrate was diluted with methylene chloride and concentrated. The residue was subjected to column chromatography (Moving phase: ethyl acetate/methylene chloride=1/7→ 1/1, v/v) to give 0.3g of the pure title compound.

¹H NMR(200MHz, CDCl₃) : δ 8.49(d, 1H, J=5Hz), 7.75(d, 1H, J=5Hz), 6.0~6.06(m, 1H), 5.45(br s, 2H), 4.15~4.55(m, 1H), 3.46(br s, 1H), 1.53(dd, 3H, J₁=25Hz, J₂=6Hz)

Example 7: Synthesis of erythro-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-4-chloro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide

Erythro-4-chloro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide (0.5g) was dissolved in acetonitrile(10ml) and phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate(0.86g) was added thereto at room temperature. DBU(0.48g) was slowly added and the reaction solution was stirred for 30minutes, diluted with methylene chloride(100ml) and washed with 5% aqueous hydrochloric acid solution(50ml). The organic layer was dried (MgSO₄), filtered and concentrated. The residue was recrystallized from diethylether/n-hexane to give 0.61g of the pure title compound as a white solid.

m.p. : 135~140°C

¹H NMR(200MHz, CDCl₃) : δ 13.2(br s, 1H), 8.63(d, 1H, J=5Hz), 7.45(d, 1H, J=5Hz), 7.2~7.4(m, 2H), 5.81(s, 1H), 4.82~5.22(m, 1H), 3.97(s, 6H), 1.44(dd, 3H, J₁=25Hz, J₂=6Hz)

Example 8: Synthesis of erythro-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-4-bromo-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide

Erythro-4-bromo-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide (0.82g) and phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate(0.86g) were reacted according to the same procedure as Example 7 to give 0.85g of the title compound as a
5 white solid.

m.p. : 87-89°C

¹H NMR(200MHz, CDCl₃) δ 8.49(d, 1H, J=5Hz), 7.65(d, 1H, J=5Hz), 7.23(s, 1H), 7.02-7.1(m, 1H), 5.80(s, 1H), 5.22-5.58(m, 1H), 4.13(s, 2H), 3.96(s, 6H), 3.41(s, 3H),
10 1.48(dd, 3H, J₁=25Hz, J₂=6Hz)

Example 9: Synthesis of erythro-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-4-methyl-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide

15 Erythro-4-methyl-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide (0.73g) and phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate(0.86g) were reacted according to the same procedure as Example 7 to give 0.75g of the title compound as a white solid.

20 m.p. : 156-158°C

¹H NMR(200MHz, CDCl₃) δ 8.58(d, 1H, J=5Hz), 7.23(d, 1H, J=5Hz), 7.21 (br s, 1H), 6.65-6.75(m, 1H), 5.78(s, 1H), 5.05-5.38(m, 1H), 4.13(s, 2H), 3.97(s, 6H), 3.41(s, 3H), 2.89(s, 3H), 1.47(dd, 3H, J₁=25Hz, J₂=6Hz)

25 **Example 10: Synthesis of erythro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide and threo-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide**

1:1 mixture of erythro and threo isomers of N-t-butyl-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide(5.0g) was dissolved in trifluoroacetic
30

acid(20ml). The reaction solution was stirred for 12 hours at 45 °C and concentrated under reduced pressure. The residue was dissolved in methylene chloride, which was then washed with aqueous sodium bicarbonate solution. The organic layer was dried over anhydrous magnesium sulfate and the residue was subjected to column chromatography (Moving phase: ethyl acetate/methylene chloride=1/7→ 1/1, v/v) to give 1.0g of the title compound in the pure erythro form and 1.0g of the title compound in the pure threo form, respectively, as a solid.

Erythro compound.

¹H NMR(200MHz, CDCl₃) : δ 8.82-8.85(m, 1H), 8.35-8.38(m, 1H), 7.43-7.50 (m, 1H), 6.60-6.72(m, 1H), 5.68(brs, 2H), 4.93-5.29(m, 1H), 4.18(s, 2H), 3.2(s, 3H), 1.55(dd, 3H, J_{H-H}=6.5Hz, J_{H-F}=25Hz),

Threo compound

¹H NMR(270MHz, CDCl₃) : δ 8.82-8.85(m, 1H), 8.35-8.38(m, 1H), 7.43-7.50 (m, 1H), 6.60-6.72(m, 1H), 5.58(brs, 2H), 5.29-5.40(m, 1H), 4.18(s, 2H), 3.43(s, 3H), 1.20(dd, 3H, J_{H-H}=6.5Hz, J_{H-F}=25Hz)

Example 11: Synthesis of erythro-2-(2-fluoro-1-hydroxyacetoxy-n-propyl)pyridine-3-sulfonamide

Erythro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide(0.5g) was dissolved in chloroform(10ml), iodotrimethylsilane(0.9ml) was added thereto, and the resulting mixture was stirred for 12 hours at 60 °C. The reaction solution was concentrated and the residue was subjected to C18 silica(50ml) column chromatography (Moving phase: CH₃CN/H₂O=10/90, v/v) to give 0.22g of the title compound.

m.p. : 142-143 °C

¹H NMR(200MHz, D₂O) : δ 8.82-8.85(m, 1H), 8.35-8.38(m, 1H), 7.43- 7.50(m, 1H), 5.0-5.4(m, 1H), 4.4(d, 2H), 1.55(dd, 3H)

Example 12: Synthesis of erythro-2-(2-fluoro-1-(3-methoxypropion)oxy-n-propyl)pyridine-3-sulfonamide

5 Erythro-N-t-butyl-2-(2-fluoro-1-(3-methoxypropion)oxy-n-propyl)pyridine-3-sulfonamide(5.0g) was reacted according to the same procedure as Example 10 to give 2.0g of the title compound.

¹H NMR(200MHz, CDCl₃) : δ 8.82-8.85(m, 1H), 8.35-8.38(m, 1H), 7.43-7.50 (m, 1H), 6.60-6.72(m, 1H), 5.75(brs, 2H), 4.93-5.29(m, 1H), 3.62(t, 2H), 3.3(s, 3H), 2.7(m, 2H), 1.55(dd, 3H)

Example 13: Synthesis of erythro-2-(2-fluoro-1-(3-hydroxypropion)oxy-n-propyl)pyridine-3-sulfonamide

15 Erythro-2-(2-fluoro-1-(3-methoxypropion)oxy-n-propyl)pyridine-3-sulfonamide (0.56g) was reacted according to the same procedure as Example 11 to give 0.12g of the title compound.

20 ¹H NMR(200MHz, D₂O) : δ 8.8(m, 1H), 8.4(m, 1H), 7.45(m, 1H), 6.9(brs, 2H), 6.75(m, 1H), 5.0-5.3(m, 1H), 3.8(m, 2H), 2.6(t, 2H), 1.55(dd, 3H)

Example 14: Synthesis of erythro-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide

25 Erythro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide(3.9g) was dissolved in acetonitrile(20ml), phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate (3.57g) was added, and then triethylamine(1.32g) was slowly added thereto. The reaction solution was stirred for 2 hours, diluted with methylene chloride(20ml) and then washed with 5% aqueous hydrochloric acid solution(10ml) and water(10ml). The organic layer

was dried over magnesium sulfate, filtered and concentrated. The residue was recrystallized from ethyl acetate/hexane/diethylether to give 4.5g of the title compound.

m.p. : 175-177°C

5 ¹H NMR(200MHz, CDCl₃) : δ 13.2(br, 1H), 8.8(m, 1H), 8.6(m, 1H), 7.5(m, 1H), 7.2(br, 1H), 6.6(m, 1H), 5.80(s, 1H), 5.0-5.3(m, 1H), 4.05(s, 2H), 3.96(s, 6H), 3.25(s, 3H), 1.45(dd, 3H)

10 **Example 15: Synthesis of threo-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide**

Threo-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide (1.56g) and phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate(2.99g) were reacted according to the same procedure as Example 14 to give 1.8g of the title compound as a white solid.

15

m.p. : 152-154°C

¹H NMR(200MHz, CDCl₃) : δ 13.2(br, 1H), 8.81(m, 1H), 8.67(m, 1H), 7.50(m, 1H), 7.49(br, 1H), 6.67(m, 1H), 5.80(s, 1H), 5.0-5.3(m, 1H), 4.05 (s, 2H), 3.96(s, 6H), 3.25(s, 3H), 1.28(dd, 3H)

20

Example 16: Synthesis of erythro-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-2-(2-fluoro-1-hydroxyacetoxy-n-propyl)pyridine-3-sulfonamide

25 Erythro-2-(2-fluoro-1-hydroxyacetoxy-n-propyl)pyridine-3-sulfonamide(1.2g) and phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate(1.33g) were reacted according to the same procedure as Example 14 to give 1.5g of the title compound as a white solid.

m.p. : 157-158°C

30 ¹H NMR(200MHz, CDCl₃) : δ 8.8(m, 1H), 8.05(m, 1H), 7.5(m, 1H), 6.7-6.8(m, 1H), 5.80(s, 1H), 5.0-5.3 (m, 1H), 4.2(m, 2H), 3.95(s, 6H), 1.45(dd, 3H)

Example 17: Synthesis of erythro-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-2-(2-fluoro-1-(3-hydroxypropion)oxy-n-propyl)pyridine-3-sulfonamide

5 Erythro-2-(2-fluoro-1-(3-hydroxypropion)oxy-n-propyl)pyridine-3-sulfonamide (0.11g) and phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate(0.18g) were reacted according to the same procedure as Example 14 to give 0.13g of the title compound.

m.p. : 147-148 °C

10 ¹H NMR(200MHz, CDCl₃) : δ 13.3(br, 1H), 8.8(m, 1H), 8.65(m, 1H), 7.6(m, 1H), 7.3(br, 1H), 5.80(s, 1H), 5.0-5.3(m, 1H), 3.96(s, 6H), 3.6-3.9 (m, 2H), 3.4(br, 1H), 2.6(m, 2H), 1.45(dd, 3H)

Example 18: Synthesis of erythro-N-[(4,6-dimethoxypyrimidin-2-yl)amino carbonyl]-2-(2-fluoro-1-(3-methoxypropion)oxy-n-propyl)pyridine-3-sulfonamide

Erythro-2-(2-fluoro-1-(3-methoxypropion)oxy-n-propyl)pyridine-3-sulfonamide (0.29g) and phenyl (4,6-dimethoxypyrimidin-2-yl)carbamate(0.53g) were reacted according to the same procedure as Example 14 to give 0.35g of the title compound.

20 m.p. : 145-146 °C

¹H NMR(200MHz, CDCl₃) : δ 8.8(m, 1H), 8.6(m, 1H), 7.5 (m, 1H), 7.2(br, 1H), 6.6(m, 1H), 5.80(s, 1H), 4.95-5.25(m, 1H), 3.95(s, 6H), 3.45(t, 2H), 3.2(s, 3H), 2.5(m, 2H), 1.5(dd, 3H)

Example 19

Herbicidal activities of the compounds according to the present invention and the known standard compounds as represented in the following Table 2 were estimated in a greenhouse.

[Table 2]

Compound of the present invention	Structure	Standard Compound	Structure
1		A	
2		B	
3		C	
4		D	
5		E	
6			
7			

Among the compounds, the standard compound E is Pyrazosulfuron-ethyl, which
30 is the most widely used herbicide in rice at the present time. The standard compounds A,

B, C and D have similar structure to the compound of formula (1) of the present invention, and were filed already.

[Table 3a]

5 Herbicidal activity and phytotoxicity of the standard compounds in a paddy condition.

Standard Compound	<i>Oryza sativa</i>			<i>Echinochloa crus-galli</i>		
	Rate (g/ha)	Seed	Trans-planted	Rate (g/ha)	Pre-emergence	Post-emergence (3-Leaf stage)
A	80	80	70	30	100	100
	40	50	40	20	100	95
	20	40	30	10	100	90
	10	40	20	5	60	60
B	80	70	60	30	100	100
	40	50	40	20	100	90
	20	40	20	10	100	90
	10	30	20	5	50	50
C	80	70	50	30	100	100
	40	30	30	20	100	100
	20	20	20	10	100	90
	10	10	10	5	40	60
D	80	60	50	30	100	100
	40	30	20	20	100	100
	20	20	10	10	100	90
	10	10	0	5	30	50
E (Pyrazosulfu ron-ethyl)	80	30	10	30	30	20
	40	20	0	20	20	0
	20	10	0	10	10	0
	10	0	0	5	0	0

As shown in Table 3a, the standard compound E, at 80 g/ha which is the four-times higher rate than the conventional application rate (20 g/ha), shows little phytotoxicity to rice; 10 or 30% to the transplanted or direct-seeded rice, respectively. Therefore, the compound E is considered to be highly safe to rice. However, it shows weak herbicidal activity to barnyardgrass (10% at 20g/ha), which is the most important weed in rice.

On the contrary, the standard compounds A to D show excellent activity to barnyardgrass, i.e., 95% or greater activity at 20g/ha by pre- or post-emergence treatments. These compounds (A~D) also show rice safety at 20 g/ha; 10 to 40% of phytotoxicity

The compounds of the present invention have excellent herbicidal activity to barnyardgrass as well as improved rice selectivity. As shown in Table 3b, the compounds of the present invention have excellent herbicidal activity against barnyardgrass; 90% or greater depending on the compounds at 20g/ha. Further, they show acceptable rice safety at 80g/ha (30% or less), which is comparable to the standard compound E.

Weed spectrum in paddy field

Pots having a surface area of 500cm² were filled with the soil in a muddy state as mentioned above. Seeds of annual weeds such as *Monochoria vaginalis* (MOOVA), *Lindernia procumbens* (LIDPR), *Rotala indica* (ROTIN), *Scirpus juncoides* (SCPJU), etc. were sown on the surface layer of soil, and then were planted tubers of perennial weeds such as *Cyperus serotinus* (CYPSE) and *Sagittaria pygmaea* (SAGPY) in a depth of 1cm, and *Eleocharis kuroguwai* (ELOKU) and *Sagittaria trifolia* (SAGTR) in a depth of 4cm. After 5 days, the chemicals were formulated as mentioned above and applied by dropping to the water surface of the pots. The test plants were observed for two weeks after the treatment and the results are given in the following Table 4.

[Table 4]

Weed spectrum of the compounds of the present invention in a paddy condition.

Compound	Rate (g/ha)	Annual weeds				Perennial weeds			
		MOOVA	LIDPR	ROTIN	SCPJU	CYPSE	SAGPY	ELOKU	SAGTR
Com. 2	20	100	100	100	100	100	95	95	90
Com. 4	20	100	100	100	100	100	90	95	85

20

From the results of Table 4; the compounds of the present invention show high activities on various annual and perennial weeds in addition to barnyardgrass.

Consequently, the compounds of the present invention, novel herbicidal molecules in paddy conditions, effectively control the annual and perennial weeds including barnyardgrass by pre- and post-emergence treatment and provide a high level of safety to transplanted and direct-seeded rice. Therefore, they are expected to be used for such

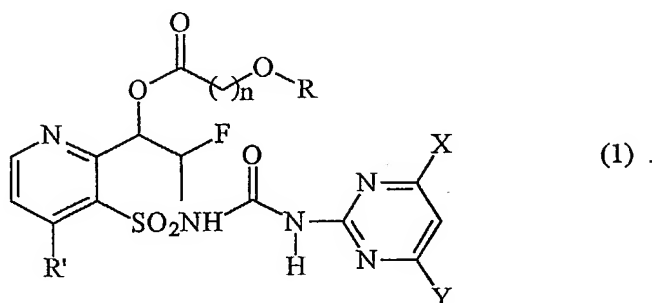
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purposes.

Claims:

1. A pyridine sulfonyl urea derivative of the following formula (1):



5

in which

n denotes an integer of from 1 to 3,

R represents H or C₁-C₄-alkyl,

R' represents H, C₁-C₄-alkyl, C₁-C₃-haloalkyl, halogen, or C₁-C₂-alkoxy, and

10

X and Y independently of one another represent C₁-C₂-alkyl, C₁-C₂-alkoxy, C₁-C₂-haloalkoxy, or halogen, salts or stereochemical isomers thereof.

2. The derivative of claim 1 wherein n denotes an integer of 1 or 2, R represents H or methyl, R' represents H, halogen or methyl, and X and Y each represents methoxy.

15

3. The derivative of claim 1 wherein n denotes an integer of 1 or 2, R represents methyl, R' represents H, Cl, Br or methyl, and X and Y each represents methoxy.

4. The derivative of claim 1 selected from the group consisting of:

20

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-methoxy acetoxy-n-propyl)pyridine-3-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-hydroxy acetoxy-n-propyl)pyridine-3-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-(3-hydroxy

propion)oxy-n-propyl)pyridine-3-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-2-(2-fluoro-1-(3-methoxypropion)oxy-n-propyl)pyridine-3-sulfonamide;

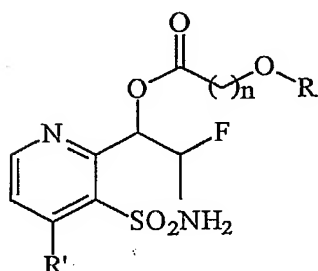
N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-4-methyl-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide;

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-4-chloro-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide; and

N-[(4,6-dimethoxypyrimidin-2-yl)aminocarbonyl]-4-bromo-2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide.

5. The derivative of claim 1 which is present in the stereoisomeric form of erythro.

6. A compound of the following formula (6):



(6)

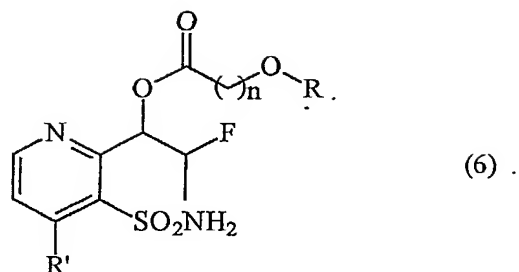
in which

n , R and R' are defined as in claim 1.

7. The compound of claim 6 which is 2-(2-fluoro-1-methoxyacetoxy-n-propyl)pyridine-3-sulfonamide.

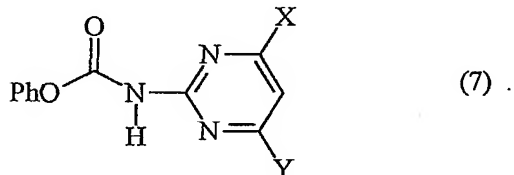
8. A process for preparing the compound of formula (1) as defined in claim 1 characterized in that a compound of the following formula (6):

32



in which

n, R and R' are defined as in claim 1, is reacted in a solvent optionally in the presence of a base with a compound of the following formula (7):



in which

X and Y are defined as in claim 1.

10

9. The process of claim 8 wherein the base is triethylamine, hexamethylenetetramine, pyridine, 1,8-diazabicyclo[5,4,0]undec-7-ene (DBU) or 1,4-diazabicyclo[2,2,2]octane (DABCO).

15

10. A herbicidal composition for controlling weeds which comprises as an active ingredient the compound of formula (1) as defined in claim 1 together with carriers.

11. The composition of claim 10 which comprises the compound of formula (1) wherein n denotes an integer of 1 or 2, R represents H or methyl, R' represents H, halogen or methyl, and X and Y each represents methoxy.

20

12. Method to use of the compound of formula (1) as defined in claim 1 for controlling weeds against rice or wheat in paddy field or upland field condition.

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Boston, Massachusetts 02209

Docket No. 57167 (71970)

DECLARATION AND POWER OF ATTORNEY

As a below named inventor, I hereby declare that: My residence, post office address and citizenship are as stated below next to my name. I believe I am the original, first and sole inventor (if only one name is listed at 201) below or an original, first and joint inventor (if plural names are listed at 201-206 below) of the subject matter which is claimed and for which a patent is sought on the invention entitled:

which is described and claimed in:

☐ the specification attached hereto.

☐ the specification in U.S. Application Serial Number _____, filed on _____.

☒ the specification in PCT international application Number, PCT/KR00/01138
filed on October 12, 2000; and was amended on _____.

I hereby state that I have reviewed and understand the contents of the above identified specification, including the claims, as amended by any amendment referred to above. I acknowledge the duty to disclose information which is material to the examination of this application in accordance with Title 37, Code of Federal Regulations, §1.56(a). I hereby claim foreign priority benefits under Title 35, United States Code, §119 of any foreign application(s) for patent or inventor's certificate listed below and have also identified below any foreign application for patent or inventor's certificate having a filing date before that of the application on which priority is claimed.

Prior Foreign/PCT Applications and Any Priority Claims Under 35 U.S.C. §119:			
Application No.	Filing Date	Country	Priority Claimed Under 35 U.S.C. §119?
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO
			<input type="checkbox"/> YES <input type="checkbox"/> NO

I hereby claim the benefit under 35 U.S.C. §120 of any United States application(s) or PCT international application(s) designating the United States of America that is/are listed below, and, insofar as the subject matter of each of the claims of this application is not disclosed in that/those prior application(s) in the manner provided by the first paragraph of 35 U.S.C. §112, I acknowledge the duty to disclose material information as defined in 37 CFR §1.56(a) which occurred between the filing date of the prior application(s) and the national or PCT international filing date of this application:

Prior U.S. Applications or PCT International Applications Designating the U.S.-Benefit Under 35 U.S.C. §120				
U.S. Applications		Status (Check One)		
Application Serial No.	U.S. Filing Date	Patented	Pending	Abandoned
PCT Applications Designating the U.S.				
Application No.	Filing Date	U.S. Serial No. Assigned		

CLAIM FOR BENEFIT OF PRIOR U.S. PROVISIONAL APPLICATION(S)
(35 U.S.C. §119(e))

I hereby claim the benefit under Title 35, United States Code, §119(e) of any United States provisional application(s) listed below:

Applicant	Provisional Application Number	Filing Date

POWER OF ATTORNEY: As a named inventor, I hereby appoint the following attorney(s) with full powers of association, substitution and revocation to prosecute this application and transact all business in the Patent and Trademark Office connected therewith.

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Linda M. Buckley	(Reg. No. <u>31,003</u>)	David A. Tucker	(Reg. No. <u>27,840</u>)	Edward J. Adamson	(Reg. No. <u>50,927</u>)
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(21)

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1-00 201	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
		KOO	Suk-Jin	
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	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
		CHO	Jin-Ho	
		Expo Apt. #509-601, Jumin-dong, Yusong-gu, 305-390 KRX	Taejon, Republic of Korea	Republic of Korea
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3-00 203	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
		KIM	Jeong-Su	
		Expo Apt. #410-901, Jumin-dong, Yusong-gu, 305-762 KRX	Taejon, Republic of Korea	Republic of Korea
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4-00 204	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
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5-00 205	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
		KANG	Kyung-Goo	
		Song-gang Green Apt. 317-503, Song-gang-dong, Yusong-gu, 305-751 KRX	Taejon, Republic of Korea	Republic of Korea
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	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
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7-00

207	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
	RESIDENCE & CITIZENSHIP	CITY	STATE OR FOREIGN COUNTRY	COUNTRY OF CITIZENSHIP
	POST OFFICE ADDRESS	POST OFFICE ADDRESS	CITY	STATE OR COUNTRY AND ZIP CODE
		CHANG	Hae-Sung	
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		Same as above		

8-00

208	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
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9-00

209	FULL NAME OF INVENTOR	LAST NAME	FIRST NAME	MIDDLE NAME
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		Same as above		

I hereby further declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true; and further, that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code, and that such willful false statements may jeopardize the validity of the application or any patent issued thereon.

Signature of Inventor 201 <i>[Signature]</i>	Signature of Inventor 202 <i>[Signature]</i>
Date: <i>Oct. 26, 2002</i>	Date: <i>Oct. 26, 2002</i>
Signature of Inventor 203 <i>[Signature]</i>	Signature of Inventor 204 <i>[Signature]</i>
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Signature of Inventor 209 <i>[Signature]</i>	Signature of Inventor <i>[Signature]</i>
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